

**WHAT IS CLAIMED IS:**

- 1            1. A process for the preparation of organic isocyanates, said  
2            process comprising:  
3            a) mixing an organic formamide compound or its amine and  
4            formate precursors with a diorganocarbonate to form a  
5            reaction mixture;  
6            b) subjecting said reaction mixture to an elevated temperature  
7            sufficient to generate the isocyanate corresponding to said  
8            organic formamide compound; and  
9            c) isolating said isocyanate from said reaction mixture.
- 1            2. The process of claim 1, wherein said organic formamide  
2            compound is one of the formula  
3             $R(NHCHO)_n$   
4            where n is an integer from 1 to 10 and R is an organic radical.
- 1            3. The process of claim 2, wherein R comprises an optionally  
2            substituted  $C_{1-20}$  alkyl,  $C_{2-20}$  alkenyl,  $C_{2-20}$  alkynyl,  $C_{4-20}$  cycloalkyl,  $C_{4-20}$   
3            cycloalkenyl,  $C_{6-30}$  aryl,  $C_{7-30}$  aralkyl,  $C_{7-30}$  alkaryl group, a silane or siloxane or  
4            oligomer thereof wherein formamide group(s) are bound to an Si-bound hydrocarbon  
5            linking group, and wherein each of the above R may contain one or more chain or  
6            ring heteroatoms.
- 1            4. The process of claim 2, wherein R is selected from the group  
2            consisting of optionally substituted phenyl, diphenylmethane, and tolyl groups.
- 1            5. The process of claim 4, wherein R is the 2,4-bis( $N$ -formamide)  
2            of toluene diamine.

1           6. The process of claim 1, wherein steps a) and b) are combined  
2 such that the reaction temperature of step a) is maintained at a temperature wherein  
3 isocyanate is produced directly.

1           7. The process of claim 6, wherein the temperature of steps a)  
2 and b) are in the range of 150°C to 240°C.

1           8. The process of claim 1, wherein the temperature of step a) is  
2 maintained below 190°C and at a first temperature such that no substantial  
3 production of isocyanate occurs, said process further comprising:

4           a)i) isolating an intermediate, isocyanate precursor mixture  
5 containing a carbamate group-containing reaction  
6 product, and thermolyzing said isocyanate precursor  
7 mixture at a second, higher temperature to obtain the  
8 isocyanate corresponding to said organic formamide.

1           9. The process of claim 8, wherein said isocyanate precursor  
2 reaction mixture comprises in excess of 80 mol percent of the carbamate  
3 corresponding to said organic formamide, said mol percent based on the total of  
4 mols of isocyanate, carbamates and isocyanate/carbamate contained in said  
5 isocyanate precursor reaction mixture.

1           10. The process of claim 1, wherein said diorganocarbonate is  
2 selected from aliphatic, cycloaliphatic, aryl, and mixed aliphatic/aryl or  
3 cycloaliphatic/aryl carbonates.

1           11. The process of claim 1, wherein said diorganocarbonate is  
2 diphenylcarbonate.

1           12. The process of claim 2, wherein R is aliphatic or  
2 cycloaliphatic, said process further comprising adding to said reaction mixture an  
3 effective carbamide-cleaving amount of a metal catalyst.

1                   13. The process of claim 1, wherein the ratio of mols of  
2 diorganocarbonate to organic formamide is greater than 1:1 based on mols of  
3 formamide groups.

1                   14. The process of claim 1, wherein the ratio of mols of  
2 diorganocarbonate to mols of formamide groups is 2:1 to 5:1.

1                   15. The process of claim 1, wherein one or more organic di- or  
2 polyamines, an organoformate ester, and diorganophenol carbonate comprise said  
3 reaction mixture.

1                   16. The process of claim 15, wherein said organo group of said  
2 organoformate is the same as at least one of the organo groups of said  
3 diorganocarbonate, said organo groups selected from the group consisting of C<sub>1-20</sub>  
4 aliphatic, C<sub>4-20</sub> cycloaliphatic, C<sub>6-20</sub> aryl, C<sub>7-30</sub> aralkyl, and C<sub>7-30</sub> alkaryl groups, their  
5 heteroatom substituted analogs, and mixtures thereof.

1                   17. The process of claim 15, wherein said organo groups are  
2 selected from the group consisting of C<sub>1-20</sub> alkyl, C<sub>5-8</sub> cycloalkyl, and optionally  
3 substituted C<sub>6-10</sub> aryl.

1                   18. The process of claim 15, wherein all organo groups are  
2 phenyl.

1                   19. The process of claim 15, which is a continuous process  
2 wherein organoformate is removed from said reaction mixture and recycled to said  
3 reaction mixture with additional organic di- or polyamine.

1                   20. A process for the direct manufacture of an organic isocyanate  
2 from the corresponding formamide, said process comprising:

3                   a) reacting an organic formamide containing from 1 to 10  
4 formamide groups per molecule with from 1 to about 10 mol  
5 of diorganocarbonate per mol of formamide groups to form a

6 reaction mixture, said reacting taking place at a temperature  
7 such that themolysis of products contained in said reaction  
8 mixture generates the isocyanate corresponding to said  
9 organic formamide;  
10 b) separating said isocyanate from said reaction mixture.

1 21. The process of claim 20, wherein said isocyanate separated  
2 from said reaction mixture also contains partially thermolyzed products containing  
3 carbamates corresponding to said organic formamide and/or mixed  
4 isocyanate/carbamide compounds corresponding to said organic formamide, said  
5 process further comprising:

6 b)i) further thermolyzing said partially thermolyzed  
7 products to form additional isocyanate corresponding  
8 to said organic formamide; or  
9 b)ii) returning said partially thermolyzed products to said  
10 reaction mixture; or  
11 b)iii) performing both of b)i) and b)ii).

1 22. The process of claim 20, wherein diphenylcarbonate is  
2 employed as said diorganocarbonate, reaction takes place in phenol solvent, and said  
3 isocyanate separated from said reaction mixture contains phenol and phenol formate  
4 ester, said process further comprising recycling said phenol formate ester by reacting  
5 said phenol formate ester with an organic amine corresponding to said organic  
6 formamide to form said organic formamide.

1 23. A continuous process for producing organic isocyanates, said  
2 process comprising:

3 a) reacting an aryl di- or polyformamide or an amine and  
4 formate precursor thereof, with diphenyl carbonate at a  
5 temperature at least sufficient to form a reaction mixture  
6 containing O-phenylcarbamates corresponding to said aryl di-  
7 or polyformamide;

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- b) thermolyzing all or a portion of said reaction mixture to generate an isocyanate-containing mixture comprising organic isocyanate(s) corresponding to said aryl di- or polyformamide;
- c) separating said organic isocyanate from said isocyanate-containing mixture to obtain a purified organic isocyanate, and an organic isocyanate depleted mixture c)i);
- d) separating phenol from said isocyanate-containing mixture or from said organic isocyanate-depleted mixture to form a phenol-depleted mixture d)i);
- e) separating carbamates and carbamate/isocyanates from said isocyanate-containing mixture or from said mixture c)i), or d)i) and further processing said carbamates and carbamate/isocyanates by one or both of
  - e)i) further thermolyzing to form said organic isocyanate(s) corresponding to said aryl di- or polyformamide; or
  - e)ii) cycling said carbamates and/or said carbamate/isocyanates into said reaction mixture of step a), to form a carbamate-depleted mixture e)iii)
- f) separating from one or more of said isocyanate-containing mixture, c)i), d)i), or e)iii) phenol formate ester, and
- g) optionally reacting said phenol formate ester with an organic amine to form the formamide corresponding to said organic amine.

1           24. The process of claim 23, wherein said step of thermolyzing  
2 takes place at a temperature of from 150°C to 240°C.

1           25. A process for the preparation of an O-organocarbamate, said  
2 process comprising reacting an organic formamide or its amine and formate  
3 precursors with a diorganocarbonate at a temperature below that at which significant

4 thermolysis of O-organocarbamate to isocyanate occurs, and separating said O-  
5 organocarbamate from other reaction products.

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